reduced. An incidental further simplification occurs in the procedure for deriving the equivalent parameter sets in that we can disregard those molecular point-group operations that are part of the crystallographic site symmetry. If, for example, a molecule of symmetry $2/m$ is known to occupy a special position of site symmetry $\bar{1}$, we may, in constructing the table of equivalent parameter sets $e_s, \varphi_s, \psi_s, \theta_s$, replace the true molecular point group by one of its subgroups 2 or m, leaving the inversion centre to be implied by the space-group symmetry in conjunction with the specification of the molecular coordinates.

We can illustrate this matter by referring to the example, treated explicitly above, of a molecule of symmetry $2/m$ in the space group $P2_1/c$. With the molecule in a general position, i.e. with four molecules per unit cell, we derived a list of sixteen equivalent parameter sets $e_{st}, \varphi_{st}, \psi_{st}, \theta_{st}, u_t, v_t, w_t$ in the Cheshire-group unit cell of $\frac{1}{2}\mathbf{a} \times \frac{1}{2}\mathbf{b} \times \frac{1}{2}\mathbf{c}$. If we now substitute in that list the coordinate values $u=v=w=0$, appropriate to a structure with two molecules per unit cell in special

positions of site symmetry $\bar{1}$, the sixteen parameter sets reduce to eight distinct sets occurring twice over. And these are just the eight equivalent parameter sets we could have obtained if we had considered explicitly only the molecular symmetry operations 1 and 2 (or, alternatively, 1 and m) in tabulating the molecular equivalences.

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A New Interpretation of the Fourier Coefficients of Debye-Scherrer Lines from Small Distorted Crystals

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Equations are derived which express the mean distortion and the particle size coefficient of small distorted crystals in the Fourier coefficients of broadened X-ray diffraction powder lines. To this end the distribution function $\varphi(t, L)$ for the distortions L of the cells, which are at a distance t apart, is expanded into a Fourier series and it is assumed that $\varphi(t, L) = 0$ for $|L| \geq d/2$ (d is the interplanar spacing between the reflecting planes). The sums of infinite series of Fourier coefficients of all orders of a reflexion appear in the equations. The problem of the incomplete evaluation caused by the limited number of orders which can be measured in practice is discussed. Finally, as it is assumed in this analysis that the distortion coefficient is a constant for all values of the reciprocal coordinate of the line profile, the small error introduced into the equations by this approximation is calculated.

Introduction

The method most widely used for determining particle size and strains in polycrystalline materials from X-ray diffraction line broadening is that of Warren & Averbach (1952). For small distorted crystals in which no stacking faults occur, they derived the equation

$$\log_e A_n^{re}(t) = \log_e V(t) - 2\pi^2 s_n^2 \langle L_t^2 \rangle .$$

In this equation t is a distance normal to the reflecting planes. $A_n^{re}(t)$ represents the real part of the Fourier

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transform of the intensity profile of the nth order of reflexion, $i_n(s_0)$, which has been corrected for continuous factors. $V(t)$ has the following meaning: for a crystal of volume V, $VV(t)$ is the volume common to the crystal and its 'ghost' shifted a distance t. Further, s_n is the reciprocal-lattice point coordinate, and s_0 is that with origin at the reciprocal lattice point. $\langle L_t^2 \rangle$ equals $\int \varphi(t, L) L^2 dL$ (and likewise $\langle L_t \rangle = \int \varphi(t, L) L dL$). Function $\varphi(t, L)$ is the normalized distribution function for the distortion L at the distance t. Thus $t + L$ is the distance between two cells in the distorted crystal, projected on the direction perpendicular to the reflecting planes. In the ideal crystal this distance is t. The mean values of L^2 and L depend on t and for ease of

notation this dependence is indicated by the subscript t in $\langle L_t^2 \rangle$ and $\langle L_t \rangle$. In this paper we also calculate the quantity $\langle |L_t| \rangle$ which is the mean distortion. The direction into which the distortion has taken place is left out of consideration. For example, when $\varphi(t,L)$ is symmetrical, $\langle |L_t| \rangle = \langle L_t^+ \rangle = \langle |L_t^-| \rangle$ ($+$ and $-$ denoting the two opposite directions).

The equation of Warren & Averbach is exact if $\varphi(t,L)$ is a Gaussian. If not, it gives good approximate values of $V(t)$ and $\langle L_t^2 \rangle$, provided the product of s_n and $\langle L_t^2 \rangle^{1/2}$ is small.

In this paper solutions for $V(t)$, $\langle L_t \rangle$, $\langle |L_t| \rangle$ and $\langle L_t^2 \rangle^{1/2}$ are presented for the special case that $\varphi(t,L)=0$ for $|L| \geq d/2$, where d is the interplanar spacing between the reflecting planes. In many practical cases (see e.g. Wagner & Aqua, 1964), the mean strains do not exceed the value of 0·005, while the particle sizes are smaller than 500 Å. Therefore it seems to us that the condition $\varphi(t,L)=0$ for $|L| \geq d/2$, though a restriction for the general validity of the equations to be derived, will in many practical cases be satisfied. The essential point in the calculations is that $\varphi(t,L)$, as a periodic function of L with period d, can be expressed in a Fourier series and that its Fourier coefficients are equal to those of the line profiles of the reflexions from the set of planes perpendicular to the direction of t, divided by the order-independent factor $V(t)d$. The latter can be obtained from the condition that $\varphi(t,L)=0$ for $|L|=d/2$. Strictly speaking, the equality $y(t,s_n)=A_n(t)/V(t)$, just mentioned, is not exact because it is supposed that $y(t,s)$ is independent of s, so that it may be considered to be a constant for all values of s of the line profile. ($s=$ $2\sin\theta/\lambda$ and $y(t,s_n)=\int_{-\infty}^{+\infty} \varphi(t,L) \exp(2\pi i s_n L)dL$ while $A_n(t)$ is the Fourier transform of $i_n(s_0)$. The real and imaginary parts of $A_n(t)$ are denoted by $A_n^{re}(t)$ and $A_n^{im}(t)$.) This approximation, which is always used in line profile studies, is based on the assumption that the reflexion domains in reciprocal space are very small (see, e.g. Guinier, 1956, p.499). Therefore in this paper a calculation is given of the error in $y(t,s_n)$ involved by the approximation. It will be shown that for symmetrical strain distribution functions, the error in the real part of $y(t,s_n)$ is very small.

In our equations there appear the sums of infinite series of the Fourier coefficients of all orders of reflexion. This causes the practical determination of particle size factors and averaged strains to be a delicate one. In practice, often only a small number of orders can be measured, so for reliable application it must be ascertained in some way that the desired degree of convergence is obtained.

Derivation of the equations

The following refers to small distorted crystals without stacking faults. The fundamental equations to be used in our derivations are (using the continuous represen-

tation):

$$i_n(s_0) = \int_{-\infty}^{+\infty} V(t)y(t,s) \exp(-2\pi i s_0 t)dt \qquad (1)$$

and

$$A_n(t) = \int_{-\infty}^{+\infty} i_n(s_0) \exp(2\pi i s_0 t)ds_0 . \qquad (2)$$

Now by definition of

$$y(t,s) = \int_{-\infty}^{+\infty} \varphi(t,L) \exp(2\pi i s L)dL \qquad (3)$$

and using the approximation

$$V(t)y(t,s_n) = A_n(t) \qquad (4)$$

we have

$$A_n^{re}(t)/V(t) = \int_{-\infty}^{+\infty} \varphi(t,L) \cos(2\pi n L/d)dL \qquad (5)$$

and

$$A_n^{im}(t)/V(t) = \int_{-\infty}^{+\infty} \varphi(t,L) \sin(2\pi n L/d)dL . \qquad (6)$$

Introducing the hypothesis

$$\varphi(t,L)=0 \quad \text{for} \quad |L| \geq d/2 ,$$

the integration limits of (5) and (6) can be changed into $-d/2$ and $+d/2$.

Developing $\varphi(t,L)$ into a Fourier series:

$$\varphi(t,L) = a_0 + 2 \sum_{n=1}^{\infty} a_n \cos(2\pi n L/d)$$
$$+ 2 \sum_{n=1}^{\infty} b_n \sin(2\pi n L/d) . \qquad (7)$$

Because of the change of integration limits just mentioned,

$$a_n = A_n^{re}(t)/(V(t)d) \qquad (8)$$

and

$$b_n = A_n^{im}(t)/(V(t)d) . \qquad (9)$$

Then, substitution of (8) and (9) into (7), together with

$$a_0 = 1/d \int_{-d/2}^{+d/2} \varphi(t,L)dL = 1/d ,$$

gives

$$\varphi(t,L) = 1/d + \{2/[dV(t)]\} \sum_{n=1}^{\infty} [A_n^{re}(t) \cos(2\pi n L/d)$$
$$+ A_n^{im}(t) \sin(2\pi n L/d)] . \qquad (10)$$

It must be remarked that the last equation does not hold for crystals without distortions, no more is it valid for $t=0$. In both cases the distribution function $\varphi(t,L)$ is a Dirac function for which the series development cannot be made. Equation (10) can also be derived from the equations of Eastabrook & Wilson (1952)

by putting $P(m,e)=0$ for $|e| \geq 1/2m$ in their equations (8) and (9). Taking into account that $\varphi(t,L)=0$ for $|L|=d/2$, equation (10) gives

$$V(t)/2 = \sum_{n=1}^{\infty} (-1)^{n+1} A_n^{re}(t) . \quad (11)$$

With the aid of (10) $\langle |L_t| \rangle$ can be calculated:

$$\langle |L_t| \rangle = 1/d \int_{-d/2}^{+d/2} |L| dL$$

$$+ \{2/[dV(t)]\} \int_{-d/2}^{+d/2} \sum_{n=1}^{\infty} [A_n^{re}(t) \cos (2\pi nL/d)|L|$$

$$+ A_n^{im}(t) \sin (2\pi nL/d)|L|]dL . \quad (12)$$

It can easily be shown that the order of integration and summation may be reversed, giving

$$\langle |L_t| \rangle = d/4 - \{2d/[\pi^2 V(t)]\} \sum_{n=0}^{\infty} A_{2n+1}^{re}(t)/(2n+1)^2 . \quad (13)$$

In the same way $\langle L_t \rangle$ and $\langle L_t^2 \rangle$ can be calculated:

$$\langle L_t \rangle = \{d/[\pi V(t)]\} \sum_{n=1}^{\infty} (-1)^{n+1} A_n^{im}(t)/n \quad (14)$$

and

$$\langle L_t^2 \rangle = d^2/12 - \{d^2/[\pi^2 V(t)]\} \sum_{n=1}^{\infty} (-1)^{n+1} A_n^{re}(t)/n^2 . \quad (15)$$

The error introduced into the Fourier coefficients $y(t,s_n)$ by the approximation $y(t,s_n)=A_n(t)/V(t)$, can be calculated in the following way. By substituting (3) in (1) and the result in (2), the following expression for $A_n(t)$ is obtained

$$A_n(t) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} V(t')\varphi(t',L) \exp (2\pi i s_n L)$$

$$\exp \{2\pi i s_0(L+t-t')\}dLdt'ds_0 . \quad (16)$$

Substituting u for $L+t$, (16) gives

$$A_n(t) = \int_{-\infty}^{+\infty} \exp (2\pi i s_n L)dL \int_{-\infty}^{+\infty}$$

$$\exp (2\pi i s_0 u)ds_0 \int_{-\infty}^{+\infty} V(t')\varphi(t',L) \exp (-2\pi i s_0 t')dt , \quad (17)$$

which can be written as

$$A_n(t) = \int_{-\infty}^{+\infty} V(u)\varphi(u,L) \exp (2\pi i s_n L)dL . \quad (18)$$

The error $\Delta_n(t)$ introduced into $V(t)y(t,s_n)$, when this factor is approximated by $A_n(t)$, is

$$\Delta_n(t) = \int_{-\infty}^{+\infty} \{V(t+L)\varphi(t+L,L)$$

$$- V(t)\varphi(t,L)\} \exp (2\pi i s_n L)dL . \quad (19)$$

For values of $L \ll t$:

$$\partial/\partial t \{V(t)\varphi(t,L)\} =$$

$$\{V(t+L)\varphi(t+L,L) - V(t)\varphi(t,L)\}/L \quad (20)$$

and thus

$$\Delta_n(t) = d/dt \{V(t) \int_{-\infty}^{\infty} \varphi(t,L)L \exp (2\pi i s_n L)dL\}$$

$$= d/dt \{V(t)\langle L_t \exp (2\pi i s_n L_t)\rangle\}$$

$$= d/dt \{V(t)(\langle L_t \rangle + 2\pi i s_n \langle L_t^2 \rangle$$

$$- 2\pi^2 s_n^2 \langle L_t^3 \rangle - \ldots)\} . \quad (21)$$

It will be seen from (20) and (21) that the error in the real part of $V(t)y(t,s_n)$ is practically zero for symmetrical distribution functions $\varphi(t,L)$. In the case of small distorted crystals the distribution functions are usually found to be nearly symmetrical. As $V(t)$ and $\langle |L_t| \rangle$ are derived from the cosine coefficients, the approximation $y(t,s_n)=A_n(t)/V(t)$ can in most cases be safely made. For small distortions $\langle L_t \rangle$ and small s_n, (21) can be limited to the first terms, giving

$$\Delta_n(t) = d/dt \{V(t)\langle L_t \rangle\} + 2\pi i s_n d/dt \{V(t)\langle L_t^2 \rangle\} . \quad (22)$$

In the case of unsymmetrical distribution functions the error in the cosine coefficients depends on the derivatives of $V(t)$ and $\langle L_t \rangle$. As $\langle L_t^2 \rangle$ will in practice be larger than $\langle L_t \rangle$ the error in the sine coefficients will be somewhat larger and depends on the derivatives of $V(t)$ and $\langle L_t^2 \rangle$.

The error, introduced into the calculated line profile by assuming $y(t,s)$ to be independent of s has been evaluated by Gjønnes (1959).

Table 1. *Relative errors in $V(t)$* (%) *due to series termination after the mth term for hypothetical distribution functions* $\varphi(L)$

$\varphi(L)$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
m																
1	91	62	37	−20	55	−40	22	70	0	29	72	39	10	64	46	15
2	−72	−20	2·6	−20	−6	−24	−9	−30	0	−3·2	−52	−24	−16	−26	−12	−7
3	52	−1	2·6	−10	−12	−16	4·5	4	0	3·2	32	10	0·4	8	1·1	−5·4
4	−30	−1	−6	−10	4	−14	−3·2	4	0	−1·2	−26	−10	−6	−1·2	−0·4	−5·4
5	15	6	−0·6	−6	4·6	−11	1·7	0	0	1·2	16	4	−0·8	0·2	−0·2	−5·4
6	−3	−3·6	−0·6	6	−2	−9	−1·7	0	0	−0·6	−14	−5·4	−4	0	−0·2	−5·4
7	1	−0·4	2·2	−5·4	−2·4	−8	0·7	0	0	0·6	10	1·2	−0·8	0	−0·2	−5·4

Discussion

When equations (11), (13), (14) and (15) are used for the determination of the particle size factor and the mean strains the infinite series have to be approximated with two or three terms, while in some favourable cases the approximation can be made with four or five terms. Higher orders of reflexion either cannot be measured at all, or can only be measured very inaccurately because of their small intensities or the overlapping by neighbouring reflexions. The errors in $V(t)$ and $\langle|L_t|\rangle$, involved by the approximations with a finite number of m terms have been calculated for a number of functions $\varphi(t,L)$. The following functions, applicable for all values of t have been used:

$$\varphi(L)=(1-|L|p/d)p/d,$$

with $p=8, 4, 3$ and 2 respectively (functions numbers 1, 2, 3 and 4), straight lines with $\varphi(L)=0$ for $|L| \geq d/p$;

$$\varphi(L)=3/d-48L^2/d^3,$$

(number 5), parabola, with $\varphi(L)=0$ for $|L| \geq d/4$;

$$\varphi(L)=3/2d-6L^2/d^3,$$

(number 6), parabola, with $\varphi(L)=0$ for $|L| \geq d/2$;

$$\varphi(L)=12L^2/d^3-12|L|/d^2+3/d,$$

(number 7), parabola, with $\varphi(L)=0$ for $|L| \geq d/2$;

$$\varphi(L)=(1+\cos 4\pi L/d)2/d,$$

(number 8), with $\varphi(L)=0$ for $|L| \geq d/4$;

$$\varphi(L)=(1+\cos 2\pi L/d)1/d,$$

(number 9), with $\varphi(L)=0$ for $|L| \geq d/2$;

$$\varphi(L)=2(1-2|L|/d)(1+\cos 2\pi L/d),$$

(number 10), with $\varphi(L)=0$ for $|L| \geq d/2$;

$$\varphi(L)=8/\{d[1-9\exp(-8)]\}\{\exp[-16|L|/d]-\exp(-8)\},$$

$$\varphi(L)=4/\{d[1-5\exp(-4)]\}\{\exp[-8 \ |L|/d]-\exp(-4)\},$$

$$\varphi(L)=2/\{d[1-3\exp(-2)]\}\{\exp[-4 \ |L|/d]-\exp(-2)\},$$

(numbers 11, 12 and 13), truncated exponentials, with

$$\varphi(L)=0 \text{ for } |L| \geq d/2;$$

$$\varphi(L)=k \exp(-\pi k^2 L^2),$$

for which it is assumed that $\varphi(L)$ may be considered zero for $|L| \geq p/k(2\pi)^{1/2}$; $p/k(2\pi)^{1/2}=d/2$; $p=5, 4$ and 3 respectively (numbers 14, 15 and 16). For the last three functions (truncated Gaussians) the calculations have been approximated.

The errors have been tabulated in Tables 1 and 2. Those of Table 2 are based on the supposition that $V(t)$ is exactly known.

Table 2. *Relative errors in $\langle|L|\rangle$ (%) due to series termination after the mth term for hypothetical distribution functions $\varphi(L)$*

$\varphi(L)$ m	1	2	3	4	5	6
1	37	3·3	0	0·6	−0·9	0·3
2	2·5	1	0	0·1	0·2	−0·1

The results obtained with these functions indicate that series termination after the second or third term in equation (11) can give serious errors in $V(t)$ and consequently in $\langle|L_t|\rangle$, as $V(t)$ occurs in the equation for $\langle|L_t|\rangle$. The termination effect is considerably less for the series $\sum\limits_{n=0}^{\infty} A_{2n+1}^{re}(t)/(2n+1)^2$ of equation (13).

The errors decrease when the standard deviation of the distribution function of a given type becomes larger. However, for the hypothetical strain models described by the functions 7, 8, 10 and 15 and also 2, 3, 13 and
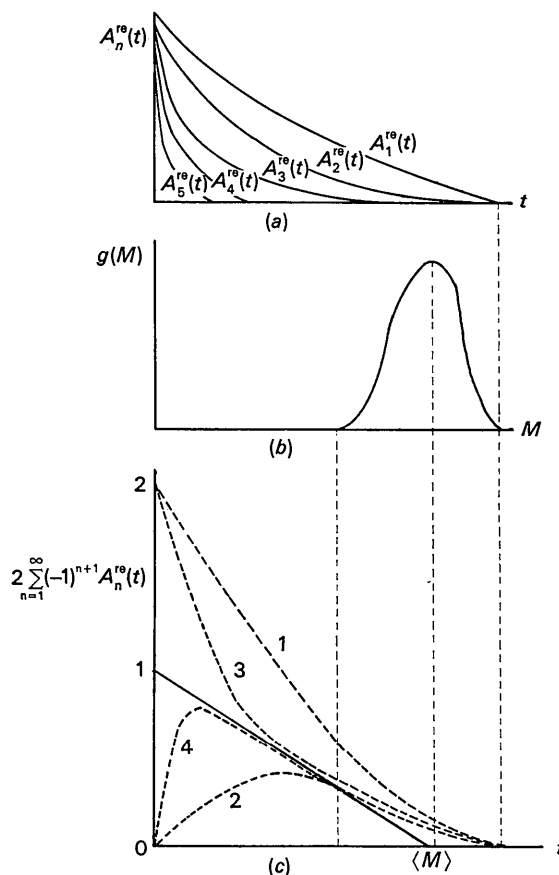

Fig. 1. (a) Fourier transforms $A_n^{re}(t)$ of the line profile of the nth order of reflexion. (b) Distribution function $g(M)$ of column lengths M. (c) Approximations of the sum $2\sum\limits_{n=1}^{\infty}(-1)^{n+1}A_n^{re}(t)$. Curve 1: $2A_1^{re}(t)$. Curve 2: $2\{A^{re}_1(t)-A_2^{re}(t)\}$. Curve 3: $2\{A_1^{re}(t)-A_2^{re}(t)+A_3^{re}(t)\}$. Curve 4: $2\{A_1^{re}(t)-A_2^{re}(t)+A_3^{re}(t)-A_4^{re}(t)\}$.

16 only small errors occur when series are not continued after the second or third term. For numbers 5 and 14 errors remain small when the series are broken off after the fourth term. Thus more than half the number of our sixteen functions give acceptable results, when using three orders of reflexion.

It is clear, that when formulae (11) and (13) are used for the determination of $V(t)$ and $\langle|L_t|\rangle$, it will be necessary to investigate if a good degree of convergence has been obtained. This can be done by comparing the result obtained with the first term with that obtained with the first and second, the latter with that of the first three terms and so on. Therefore, generally speaking, for reliable applications of these formulae it will be necessary for a rather large number of reflexion orders to be measurable.

It is impossible to determine $V(t)$ with equation (11) for small values of t, since termination errors are very large in this region. Consequently, the mean value of the column lengths perpendicular to the reflecting planes, $\langle M \rangle$, cannot be determined by applying the well-known formula

$$(dV(t)/dt)_{t\to 0} = -1/\langle M \rangle,$$

which needs values of $V(t)$ for small t. In a special case, however, we expect that $\langle M \rangle$ can be obtained in the following way. For values of t smaller than the smallest column length, $M_{\min}$, occurring in the sample,

$$V(t) = 1 - t/\langle M \rangle,$$

as is immediately evident from

$$g(M) = M(d^2V/dt^2)_{t=M}.$$

$g(M)$ is the distribution function for the column lengths M. (For these formulae see, e.g. Guinier, 1956, p. 478.)

When the $V(t)$ versus t curve, which can be derived from equation (11), partly or entirely happens to be a straight line, which after extrapolation to zero, intersects the $t=0$ axis at $V(t)=1$, $\langle M \rangle$ will be found by extrapolation of the line to the $V(t)=0$ axis (Fig. 1). In this case one can safely count on the method since the $V(t)$ versus t curve itself proves the correctness of the approximations made by the series termination. The curve will be linear for a large range of values of t when column lengths perpendicular to the reflecting planes are rather large and have a small size range.

The Fourier coefficients of the artificial functions $\varphi(L)$ gradually decrease to zero with increasing s. In some cases (numbers 1, 2, 3 and 4) they decrease to zero, rise again to a smaller maximum than the foregoing one, decrease to zero again and so on. The coefficients of 5 and 6 decrease to zero by oscillating around the $y=0$ axis with positive and negative values. In principle these oscillations have to occur also in the Fourier transforms of the line profiles, related with these artificial functions. The amplitudes of these oscillations are small and in practice it will be difficult to detect them, the more so as they occur in the region of large t, where experimental errors are largest.

The fact that only a limited number of orders of reflexion can be measured is less serious for the method of Warren & Averbach than for the method presented in this paper. The first is based on an extrapolation near $s_n = 0$ and therefore will practically always be applicable while the second only can be applied if series termination effects are small. In both cases it is not possible to decide by inspection whether the assumptions of the methods are fulfilled. Uncritical application in both cases can give values for $V(t)$ and $y(t,s_n)$ with large errors. Applying for example the Warren–Averbach method to function 13, the extrapolation to $s_n^2 = 0$ of the straight line defined by the first and second Fourier coefficients will give a value of 0·75 for $y(t,0)$ instead of 1·00 (for the functions 12, 11, 10 and 1 values of 0·80, 0·93, 1·06 and 1·01 are found respectively). The Warren–Averbach method uses mainly the Fourier coefficients at small values of t while ours uses those at larger values of t, which have larger errors caused by experimental inaccuracies (Stokes, 1948).

It seems to us that the method of Warren & Averbach will have a larger applicability, but that it is worth while to apply our method too, as, if a sufficient number of orders of reflexion can be measured, in some cases our method may give more accurate results.

Conclusion

Theoretically exact equations can be given for the particle size coefficient and the mean distortion, when the distribution functions for the distortion $\varphi(L)=0$ for values of $|L| \geq$ half the interplanar spacing. In practical applications the sums of the infinite series of the Fourier coefficients that occur in the equations have to be approximated by the sums of a limited number of terms. The errors involved by the series termination may be large. In particular cases, especially in those in which a sufficient number of orders of reflexion can be measured, it is expected that the method can give reliable results.

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